Electronic Supporting Information

Synthesis of a Pyridyl-Appended Calix[4]arene and its Application to the Modification of Silver Nanoparticles as an Fe^{3+} Colorimetric Sensor

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The procedure of synthesis of 4-propynoxypyridine

A suspension of 4-hydroxy pyridine (0.57 g, 6 mmol) and anhydrous potassium carbonate (1.66 g, 12 mmol) in acetone (20 mL) was stirred for 0.5 h at room temperature. Then a solution of 3-bromopropyne (1.3 mL, 12 mmol) dissolved in acetone (5 mL) was slowly added. The reaction mixture was stirred for 2 h at 50 °C. The cooled reaction mixture was filtered and washed with acetone. The filtrate were removed under vacuum and the residue was further purified by column chromatography eluting with ethyl acetate/methanol (v/v= 5:1); Yield: 95%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.2 Hz, 2H, PyH), 6.42 (d, *J* = 7.2 Hz, 2H, PyH), 4.60 (s, 2H, OCH_2Py), 2.65 (s, 1H, CCH).

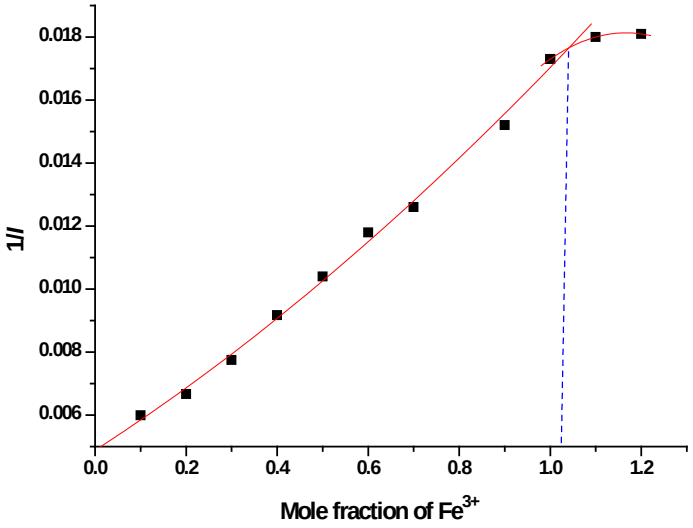


Fig. S1. The plot of 1/*I* versus mole fraction of Fe^{3+}. Fluorescence spectra of **2** (5×10^{-5} M) with various equivalents of Fe^{3+} in CH_3CN (0 -1.2 equiv).

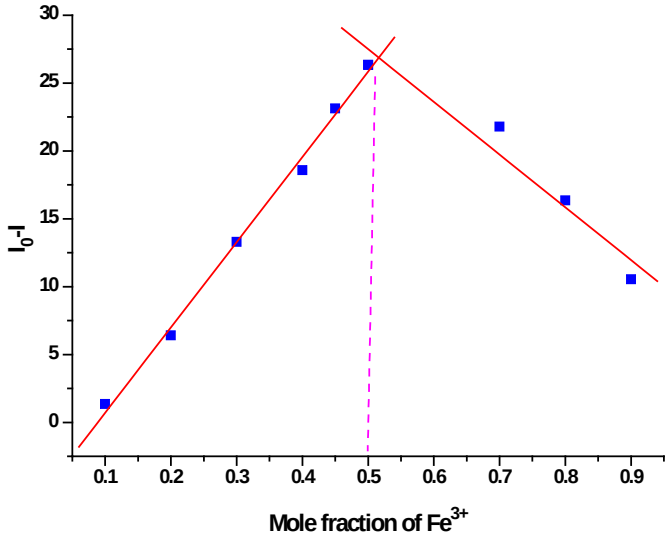


Fig. S2. Job's plots of **2** toward Fe^{3+} in CH_3CN solution at an invariant total concentration of 10^{-5} M. (Excitation 285nm)

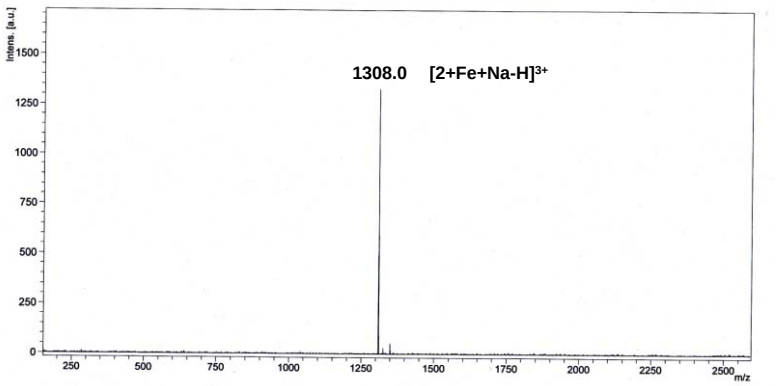


Fig. S3 The MALDI-TOF mass spectrum of the **2**·Fe^{3+} complex.

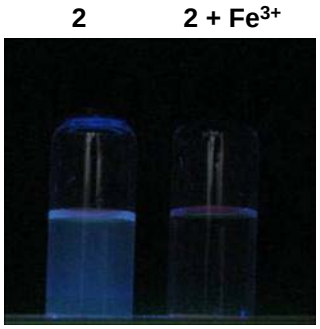


Fig. S4 Photographs of the fluorescence responses (**2** (5×10^{-4} M) in the absence and presence of 1.0 equiv Fe^{3+} in CH_3CN under UV light (λex = 254 nm).

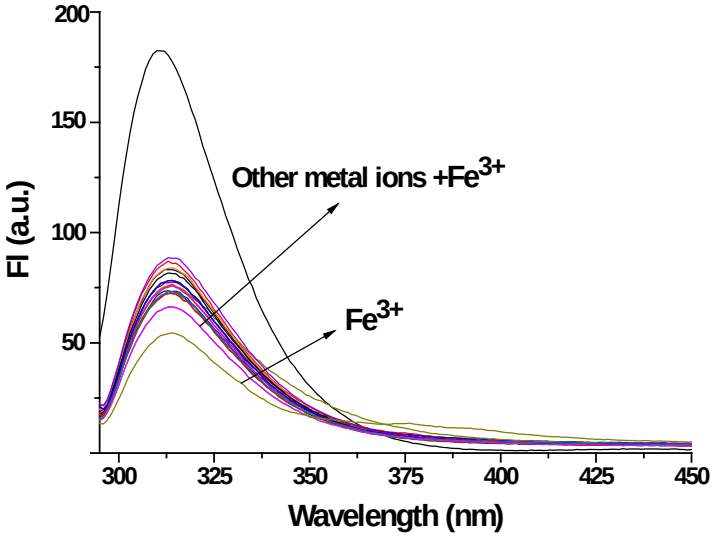


Fig. S5. The fluorescence changes of **2** (10^{-5} M) toward 5.0×10^{-5} M Fe^{3+} in the presence of 1.0×10^{-4} M other ions. I_o is fluorescence emission intensity at 313 nm for free **2,** and I is the fluorescent intensity upon addition of other metal ions with the existence of Fe^{3+}.

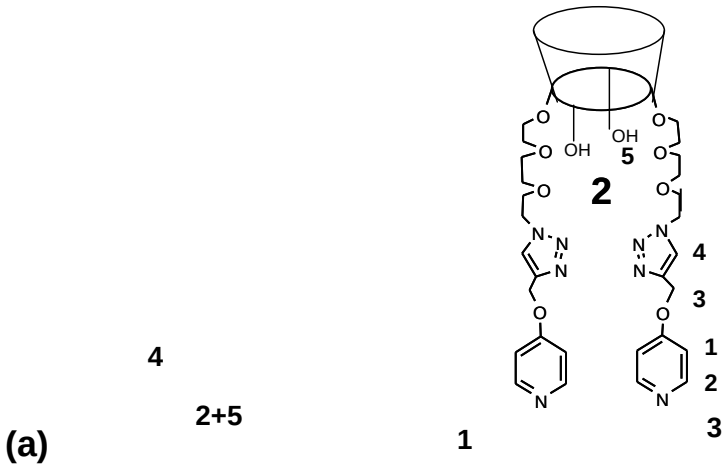


Fig. S6. The partial ^{1}H NMR spectra of (c) **2** (5 mM) in CD_3CN and in the presence of (b) 1.0 equiv and (a) 2.0 equiv of $Fe(ClO_4)_3$.

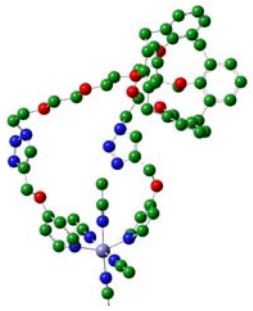


Fig. S7. The optimized structure of the **2**·Fe^{3+} complex

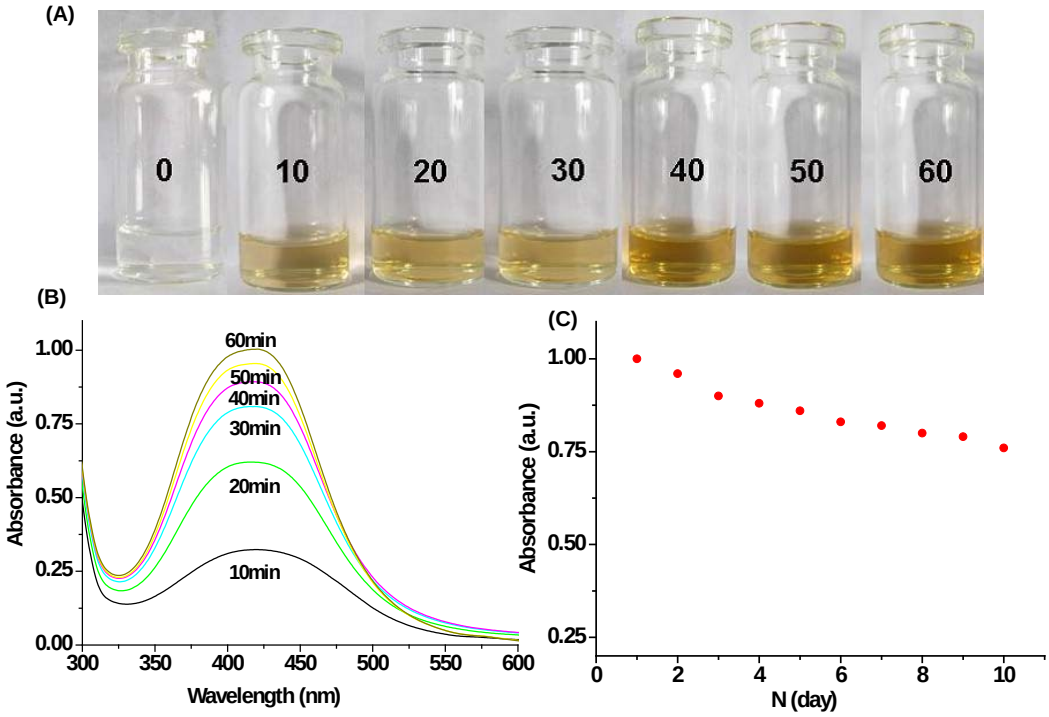


Fig. S8. The photographic images (A), UV-vis spectra (B) of **2**-Ag NPs on the increasing time (10-60 min) under the ultraviolet light at λ_{max} = 365nm. (C) The stability of the **2**-Ag NPs (the absorbance intensity at 414 nm).

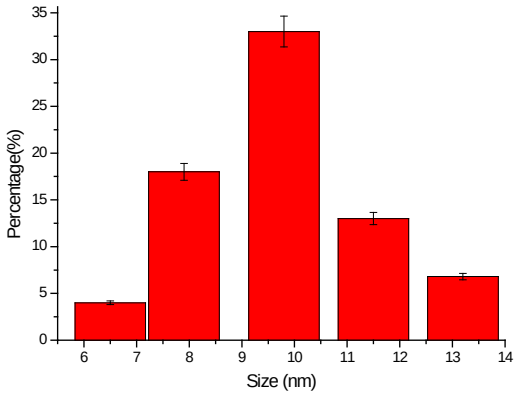


Fig. S9 Size distribution of TEM images of **2**-Ag NPs.

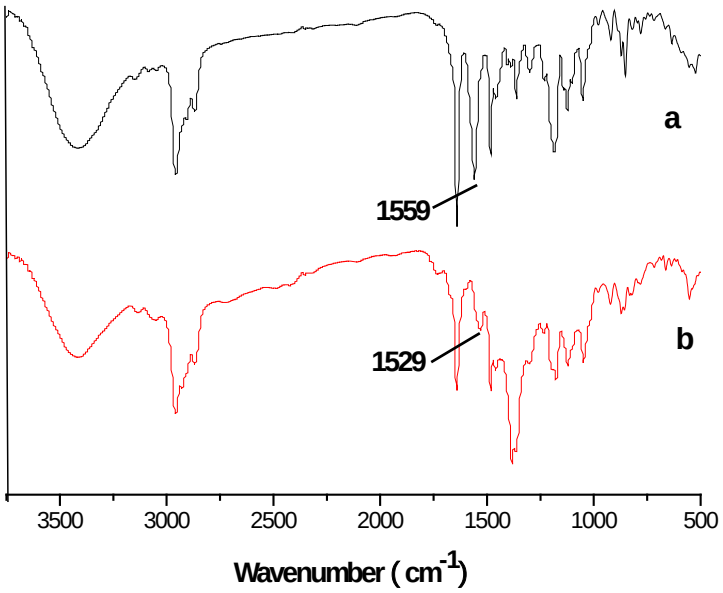


Fig. S10 FT-IR spectra of (a) calix[4]arene **2** and (b) **2**-Ag NPs

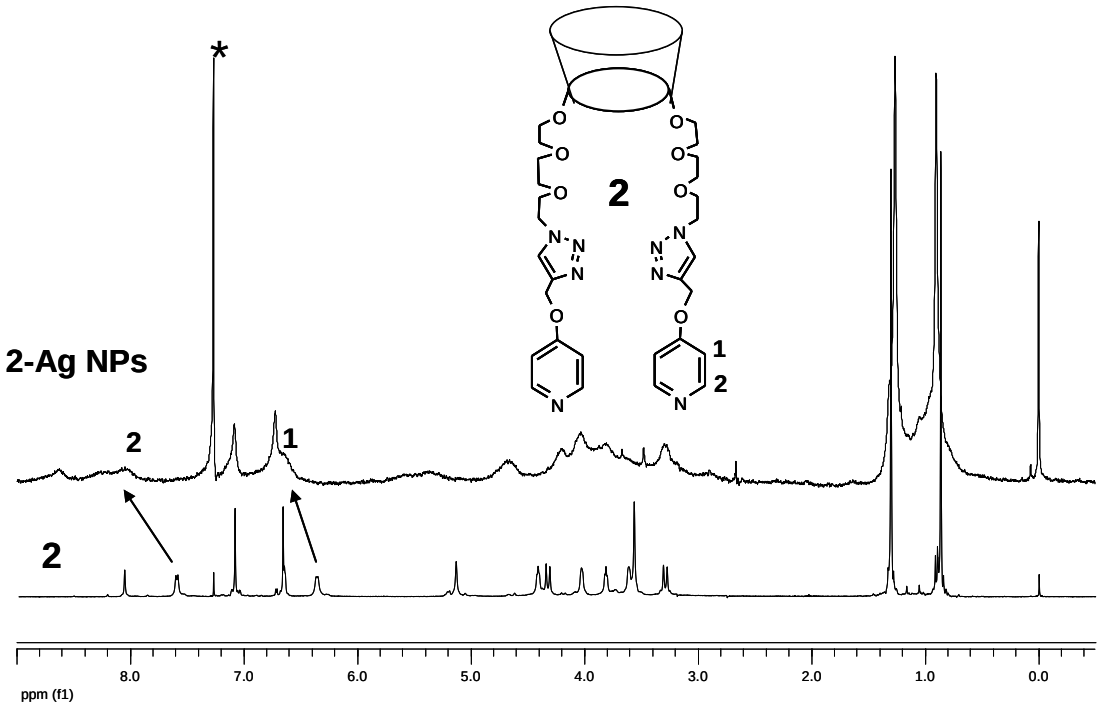


Fig. S11 ^{1}H NMR of calix[4]arene **2** and **2**-Ag NPs in $CDCl_3$.

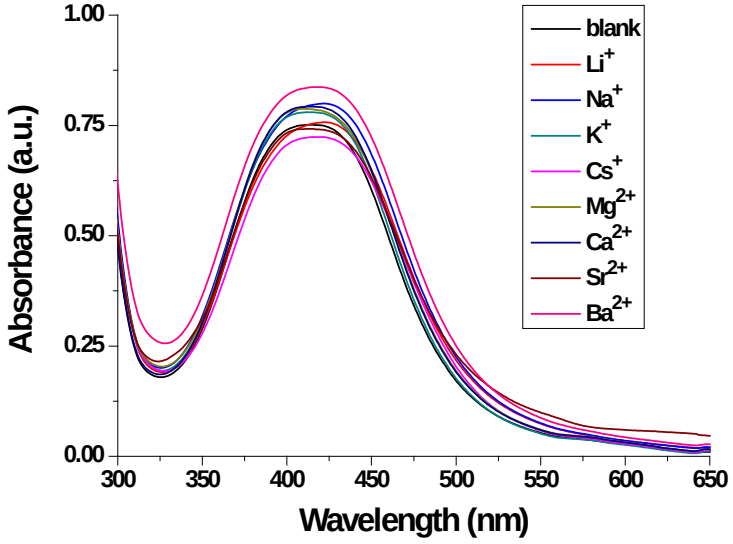


Fig. S12 The UV-vis spectra of 2-Ag NPs, in the presence of different 0.2 mM alkali metal ions and alkaline earth metal ions (Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) in methanol solutions.

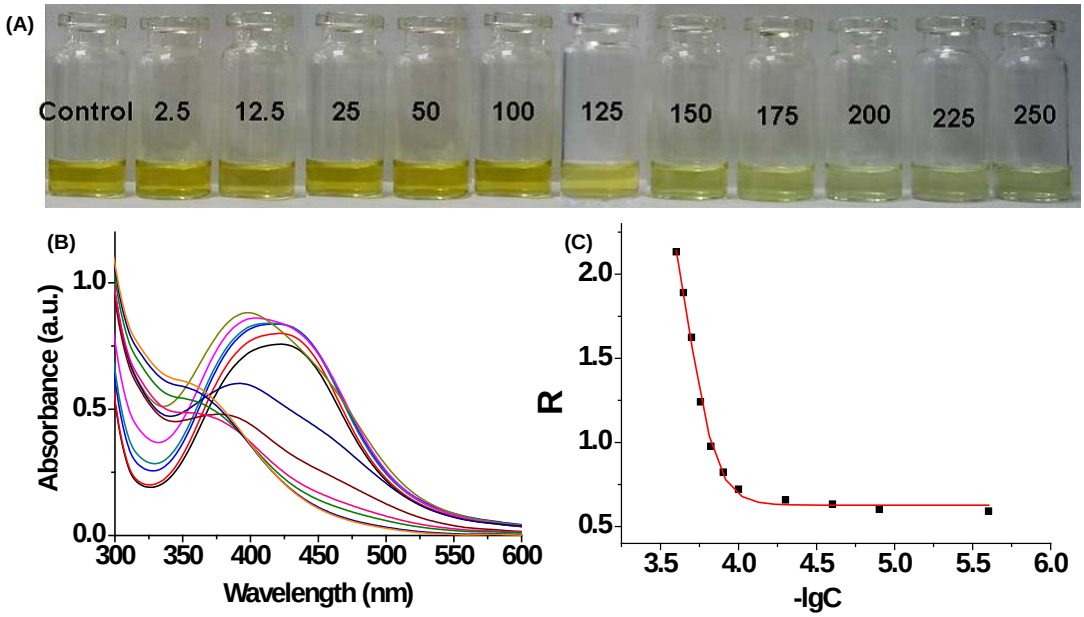
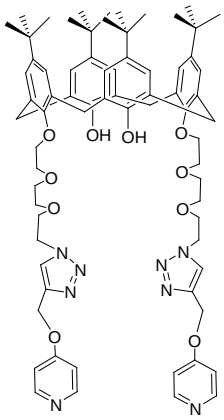
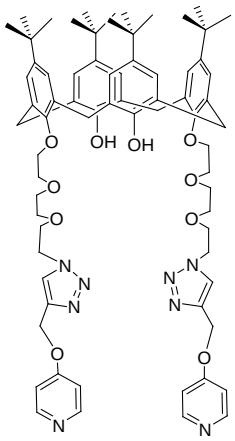


Fig. S13 The photographic images (A), UV-vis spectra (B) and the dependence of the R values (A_{364}/A_{414}) of (C) of **2**-Ag NPs on the increasing concentration of Fe^{3+} (2.5-250 μM). Typically, 0.5 mL of various concentrations of Fe^{3+} were added into 1.5 mL **2**-Ag NP solutions, and the combined solution mixed well for 30 min and then tested.





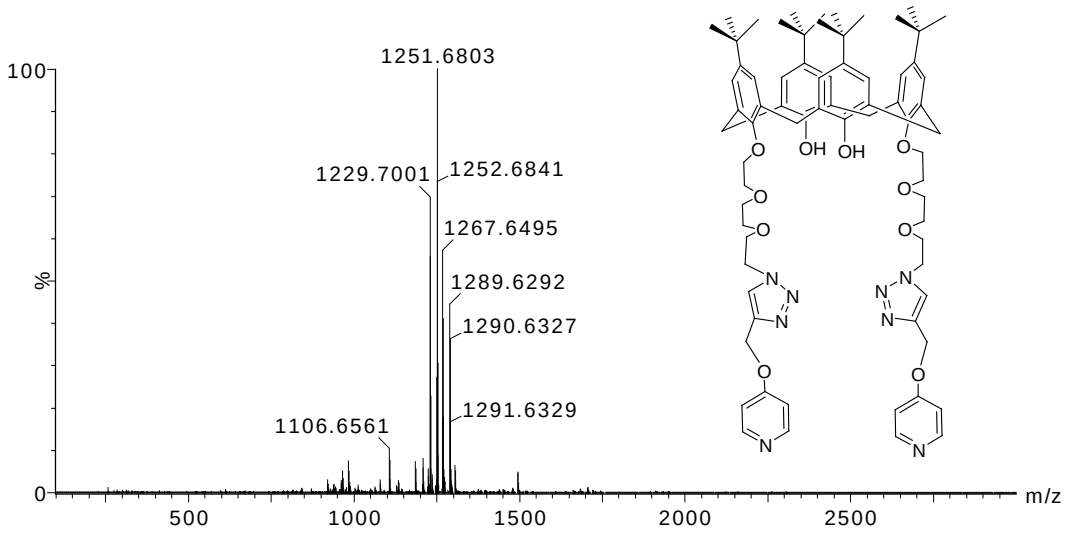


Fig. S14 NMR and HDMS spectra of compounds **2**